SUMMARY

In this thesis the results of an investigation of transition-metal ions substituted in diiodides with a layer structure are discussed. This study is carried out in order to obtain more information about the electronic state of the metal ion, which in these crystals is strongly affected by covalency, anion spin-orbit coupling, and lattice vibrations.

Chapter II deals with the anisotropy of the lattice vibrations of ionic crystals with a layer structure. The Coulomb interaction between the ions in the crystal is described by the polarizable-ion approximation. For compounds with the $Cd(OH)_2$ or $CdCl_2$ type structure relations between the macroscopic optical parameters and the force field are derived for the infrared-active vibration modes. The far-infrared reflection spectra of PbI_2, CdI_2, SnS_2, and $SnSe_2$ are analysed in terms of this model. From this analysis values are obtained for the polarizabilities of the ions, the force constants due to short-range interactions between neighbouring cations and anions, the Szigeti dynamical ionic charges, and the induced electric-dipole moments of the anion. It is found that the contribution of the short-range interactions to the force field is almost isotropic. The large anisotropy of the infrared-active vibration modes is caused for the main part by the long-range Coulomb interaction, the static dipoles of the anions playing an important role. The dynamical reduction of the ionic charges and the anion dipoles is larger in the semiconductors SnS_2 and $SnSe_2$ than for the more ionic compounds PbI_2 and CdI_2.

In chapter III the EPR spectra of single crystals of CdI_2 and PbI_2 doped with divalent vanadium, manganese, and cobalt are reported. The EPR spectra of V^{2+} and Mn^{2+} in CdI_2 and PbI_2 and of Co^{2+} in PbI_2 are analysed in terms of a spin Hamiltonian. The parameters obtained are compared with those of the same ions in $CdCl_2$, $MgCl_2$, and $CdBr_2$. The g shift of V^{2+} in PbI_2 and CdI_2 has the opposite sign of the g shift of this ion in $CdCl_2$ and $CdBr_2$. This is the result of the contribution of the iodine 5p orbitals

to the mixing between the $^4A_{2g}$ ground state and the 10 Dq excited state by spin-orbit coupling. The g values of Co^{2+} in $CdCl_2$, $CdBr_2$, and PbI_2 indicate that the trigonal ligand fields differ appreciably in these lattices. The temperature dependence of the zero-field splitting of Mn^{2+} in dihalides with a layer structure is ascribed to the anisotropy of the optical lattice vibrations. The observed temperature dependence is in good agreement with the calculated temperature dependence of the contribution of the Raman-active modes for the host lattices $CdCl_2$, $CdBr_2$, and CdI_2. The ligand hyperfine interaction between the Mn^{2+} electron spin and the iodine nuclear spin in CdI_2 is quite different than that in PbI_2.

The results of light-absorption measurements of iron ions in CdI_2 and PbI_2 are discussed in chapter IV. Transitions between electronic states of the iron $3d^6$ configuration cause Laporte-forbidden absorption bands. The absorption bands observed for iron in CdI_2, PbI_2, and FeI_2 below 18000 cm^{-1}, can be assigned by the use of a Tanabe-Sugano diagram. The spectra of CdI_2 with small iron concentrations consist of a number of narrow absorption bands above 18000 cm^{-1}, which show fine structure at low temperature. The 10 Dq band of octahedrally-coordinated Fe^{2+} is split by a strong Jahn-Teller effect of the ^5E_g excited state. The temperature dependence of this splitting for iron in CdI_2 is compared with similar data for iron in $CdCl_2$, $CdBr_2$, and CdI_2. The oscillator strengths of the spin-forbidden transitions between the $^5T_{2g}$ ground state and the excited triplet states are relatively large for iron in diiodides. This is probably caused by the large spin-orbit coupling of the iodine 5p orbitals, which contributes to the mixing between the electronic states of the $3d^6$ configuration and the charge-transfer states.